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# Synthesis and electro-optical behaviour of a new chiral smectic side-chain polysiloxane

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## *Summary*

*A new chiral side-chain polymer was prepared by hydrosilylation of a dimethylsilane-methylhydrosilane copolymer. The chiral group of the mesogenic side-chain was (+)2-chloro-3-(3-nitro-4-hydroxyphenyl)propionic acid butyl ester while the main part of the aromatic nucleus consisted of 4´-hydroxybiphenyl-4-carboxylic acid. Phase behaviour was studied by DSC and polarizing microscopy, and correlated with dielectric measurements. Alignment properties and ferroelectricity were studied in cells with surface-induced alignment and in shear cells. The polymer exhibits chiral C-and A-phases. The spontaneous polarization is 130 nC/cm$^2$ at 60°C and the polymer shows ferroelectric switching at room temperature.*

## Introduction

Organic thin films with controlled, polar orientation of functional groups are of increasing importance for microelectronic and optoelectronic applications. Different ways to achieve such structures are polar deposition of Langmuir-Blodgett layers, electrical poling of polymer films, and self-assembled multilayers. A new route to obtain polymer films with polar orientation is to take advantage of the liquid crystalline order in side-chain polymers, and in this way achieving thermodynamically stable, polar orientation of the mesogenic groups in ferroelectric liquid crystal polymers (FLCPs). The first FLCPs were reported in 1984 (1), but only recently have reasonably well characterized and orientable polymers of this type been synthesized (2-7). Due to the complexity of polymer structure, and the associated multitude of functionality options, the synthetic chemistry and physical studies of FLCPs are only in their infancy. On the other hand, since the application potential of these new polymers is very large, there is a strong driving force for basic research and development (8). Of prime importance is the synthetic effort for systematic structure variations, and the studies of the side-chain dynamics in relation to main-chain composition. In the present communication we describe synthesis, characterization and physical properties, including alignment and ferroelectric switching, of a new ferroelectric liquid crystalline side-chain polymer exhibiting broad chiral smectic A- (A*) and C- (C*) phases. The side-chains are based on 4´-hydroxybiphenyl-4-carboxylic acid and a derivative of the chiral amino acid tyrosine as aromatic nucleus and chiral group respectively. The polymer backbone is poly-(dimethylsiloxane-co-hydrogenmethylsiloxane) with a dimethylsiloxane/hydrogenmethylsiloxane ratio of 2.7:1. The alignment and optical switching properties of the polymer have been investigated and electro-optical switching at room temperature has been found.

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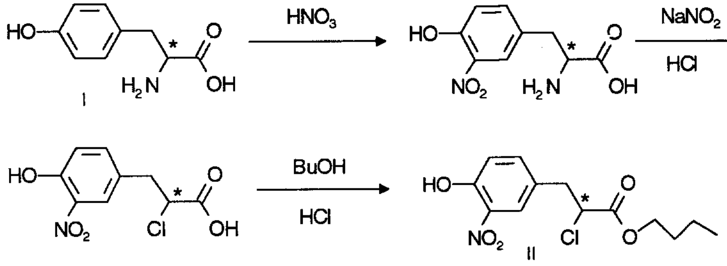
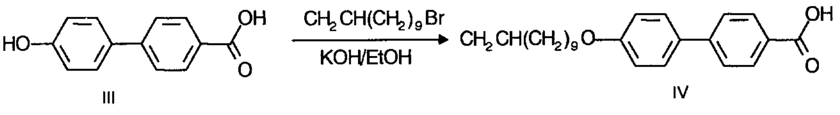
## Experimental

*Materials.* Materials and reagents were of commercial grade quality and used without further purification unless otherwise noted. Dry toluene and methylene chloride were obtained by passing the solvents through a bed of aluminum oxide (ICN Alumina N-Super I). Poly-(dimethylsiloxane-co-hydrogenmethylsiloxane) and the hydrosilylation catalyst dicyclopentadienyl-platinum(II) dichloride were obtained from Wacker Chemie AG.



**Scheme 1.** Synthesis of (+)2-Chloro-3-(3-nitro-4-hydroxyphenyl)propionic acid butyl ester.

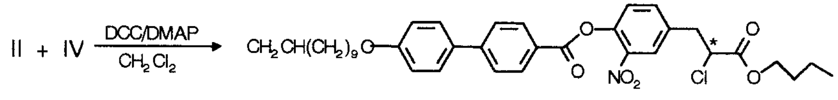
*(+)2-Chloro-3-(3-nitro-4-hydroxyphenyl)propionic acid butyl ester* (II). The synthesis of II was carried out from L(-)tyrosine (I) via nitration (9), diazotization (10) and esterification (Scheme 1) without extensive purification of the intermediate products. L(-)Tyrosine, 0.1 mol (18.1 g) was suspended in 85 mL of water and placed on an ice-bath. 30 mL of conc. nitric acid was added gently with stirring. After 1 hour the flask was covered with plastic foil and placed in the refrigerator over night. The red mixture was filtered and the isolated product was reprecipitated from 6 M hydrochloric acid to yield a yellow precipitate. The product was dissolved in 200 mL of 6 M hydrochloric acid cooled down to 0 - 5°C and diazotized with 0.1 mol (6.3 g) sodium nitrite in 20 mL of water. The reaction mixture was extracted with ether, dried over magnesium sulphate and evaporated till dryness. 2 g of the crude product was esterified in 10 mL butanol using hydrogen chloric gas as a catalyst. Excess alcohol was evaporated and the residue was purified on a silica column using petrol ether/ethyl acetate 3/1 as an eluent. The butyl ester II forms a yellow oil pure according to tlc and $^1$H NMR. $[\alpha]_D^{20}$= 8.35° (ethanol). $^1$H NMR: $\delta$ = 0.9 t 1H, $\delta$ = 1.32 m 2H, $\delta$ = 1.6 m 3H, $\delta$ = 3.18 q 1H, $\delta$ = 3.34 q 1H, $\delta$ = 4.15 m 2H, $\delta$ = 4.4 q 2H, $\delta$ = 7.1 d 1H, $\delta$ = 7.45 dd 1H, $\delta$ = 7.97 d 1H, $\delta$ = 10.55 s 0.5 H. NMR spectra of intermediate products were in accordance with their respective structure.



**Scheme 2.** Synthesis of 4′-(10-undecenyloxy)-biphenyl-4-carboxylic acid.

*4′-Hydroxy-biphenyl-4-carboxylic acid* (III) was synthesized in accordance with the method of Gray et. al. (11) from 4-hydroxybiphenyl via 4-ethoxybiphenyl, 4-acetyl-4'-ethoxybiphenyl and 4'-ethoxybiphenyl-4-carboxylic acid.

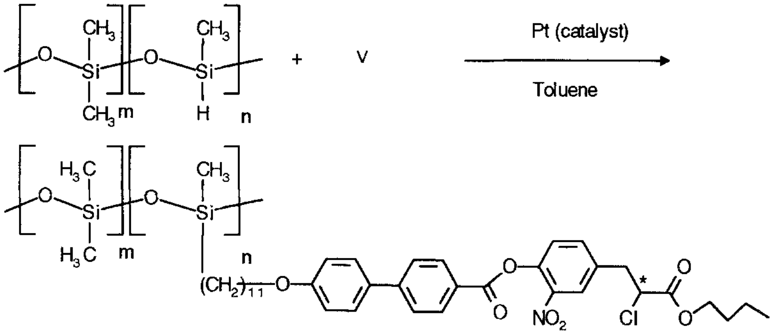
*4'-(10-Undecenyloxy)-biphenyl-4-carboxylic acid* (IV) (12). To a hot mixture of 34 mmol (7.3 g) of III and potassium hydroxide, 86%, (4.4 g) in ethanol (1.0 L) and water (100 mL), undecenyl bromide 68 mmol was added. The reaction mixture was refluxed for 12 hr and the ester was hydrolysed by adding a 10% solution of potassium hydroxide in 70% ethanol and refluxing for two hours. The product was recrystallized from acetic acid and ethanol. Yield 7.9 g (65%).



**Scheme 3.**

V

*2-Nitro-4-(3-(+)-2-chloropropionic acid butylester)-phenyl-4'-(10-undecenyloxy)-biphenyl-4-carboxylate* (V) (Scheme 3) (12). 2.5 mmol (0.92 g) of the acid IV and 2.5 mmol (0.76 g) of II were dissolved in 5 mL dry methylene chloride. Dimethylaminopyridine (DMAP) 6 mg was added and the mixture was cooled to 0°C. Dicyclohexylcarbodiimide (DCC) 0.25 g in 5 mL of methylene chloride was added dropwise. After 3 hours the temperature was raised to 20°C and stirring was continued for additionally 10 hours. The mixture was filtered and the filtrate was evaporated to dryness. Recrystallization from ethanol gave 0.57 g product, yield 70%. $[\alpha]_D^{20}$=-1.0° (chloroform). $^1$H NMR: $\delta$ = 0.92 t 3H, $\delta$ = 1.2-1.7 m 16H, $\delta$ = 1.80 m 2H, $\delta$ = 2.02 q 2H, $\delta$ = 3.58 2xdd 2H, $\delta$ = 3.98 t 2H, $\delta$ = 4.17 m 2H, $\delta$ = 4.46 t 1H, $\delta$ = 4.94 m 2H, $\delta$ = 5.80 m 1H, $\delta$ = 6.98 d 2H, $\delta$ = 7.34 d 1H, $\delta$ = 7.57 d+s 3H, $\delta$ = 7.68 d 2H, $\delta$ = 8.01 s 1H,$\delta$= 8.20 d 2H.



VI

~0°C SmC* 70°C SmA* 104°C Iso

**Scheme 4.** Attachment of side-chains.

*Polymer* (VI) (Scheme 4) (13). A dry flask containing poly(dimethylsiloxane-co-hydrogen-methylsiloxane) (2.7:1) 0.17 g (0.65 mmol counted on Si-H) and (V) 0.7 mmol (0.46 g) was evacuated and filled with nitrogen three times. Dry toluene 4 mL was added and the mixture was heated to 100°C. A solution of catalyst, dicyclopentadienyl-platinum(II)-dichloride 0.12 mg in 10 mL of toluene, was added 1 mL at a time during 2-3 days. After completion the reaction mixture was precipitated in methanol 250 mL, and the polymer was collected by centrifugation. To remove the catalyst the product was chromatographed on aluminum oxide with ethyl acetate as eluent. The polymer containing solution was microfiltered (0.2 $\mu$m) prior to reprecipitation from chloroform with methanol. $[\alpha]_D^{20} = -1.2°$. DSC results together with polarizing microscopy studies gave the phase behaviour of polymer VI shown in Scheme 4. The phase behaviour below about 0°C is not yet clarified.

**Physical characterization**

For detailed physical measurements, it is essential to obtain well aligned samples. In the geometry of fig. 1 the smectic layers are oriented perpendicular to the substrate plates and in the case of shear alignment, along the shear direction. We introduce the vectors $\hat{k}$ (smectic layer normal), $\hat{n}$ (molecular director, or average side-chain orientation), **P** (spontaneous polarization in the C*-phase) and **E** (applied electric field). The tilt angle $\theta$ is the angle between $\hat{k}$ and $\hat{n}$. The parameter $P_0$ in fig. 1 can be either positive or negative for a given substance and **P** can even change sign as a function of temperature. If we neglect boundary effects, the polarization vector is either along z or -z depending on the sign of the applied field **E**, corresponding to a molecular tilt of $\theta$ or $-\theta$ relative to the layer normal. The main-chain structure relative to the side-chains is not known in detail, but recent X-ray investigations (14) of similar side-chain polymers indicate a micro-phase separation between the siloxane backbone and the chiral side-chains. Fig. 2 indicates the situation in the smectic C* phase, but by setting $\theta=0$ it also illustrates the orthogonal A*-phase. Two different approaches are used to obtain the alignment: Either surface-induced alignment, with cells precoated with thin oriented polyimide layers, or shear-induced alignment in specially designed shear-cells. Surface-coated cells were standard commercial cells with 4 x 4 mm$^2$ active area and 4 micron thickness. The cells can be capillary filled with the polymer in 6-8 hours at 110°C, but generally produce poor alignment. Excellent alignment was obtained by shearing the sample in the smectic A*-phase close to the isotropic phase, and slowly cool it to

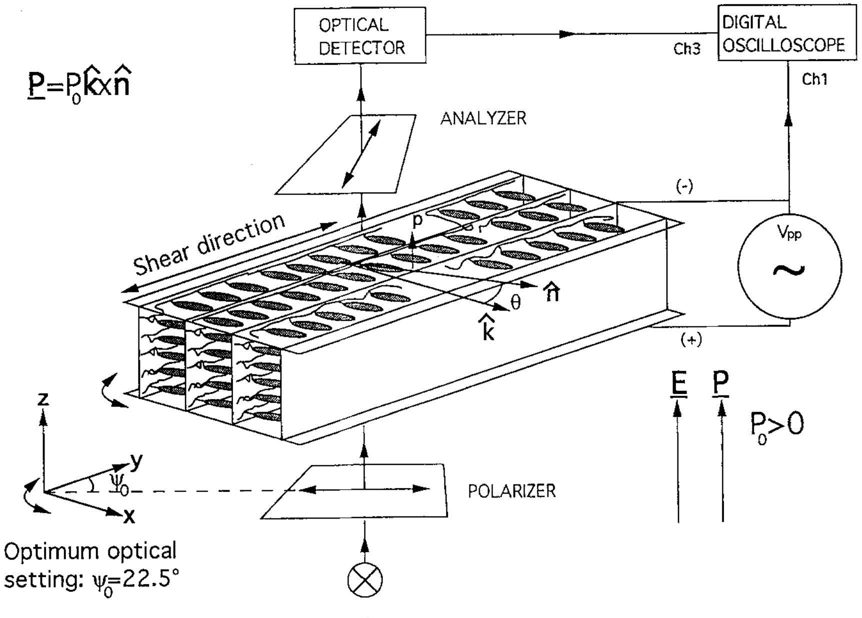


**Figure 1.** The experimental setup and cell geometry.

the smectic C*-phase. The polymer sample was prepared between two ITO-coated glass plates with a special electrode pattern in order to have a well-defined active area (16.8 mm$^2$) independent of shear position. A protective 1000 Å uniform SiO layer and SiO-spacers were deposited by normal incidence thermal evaporation. The shear orientation cell was mounted in a Mettler FP52 hot stage for temperature control, and observed in a Zeiss Photomicroscope equipped with a fast electro-optic recording system. For experimental details see ref. (15). For polymer work, the great advantage of the shear cell is that it is filled rapidly, and provides good alignment. For the determination of electric field induced tilt angles in the smectic A*-phase, the cell is observed between crossed polarizers, and positioned with the smectic layer normal oriented at an angle $\psi_0$ to the analyzer. The transmitted intensity is given by eq. 1 where $\psi=\psi_0+\theta(E)$ and $\theta$ is the field induced tilt angle. For a given thickness d and birefringence $\Delta n$ the second factor is constant, and the observed light modulation is due to $\theta(E)$, where E is the applied electric field (triangular wave form). It can be shown that for $\psi_0=22.5°$, the intensity modulation is maximal, and the field induced tilt angle can then be

$$I=I_0\sin^2 2\psi \sin^2\frac{\pi d}{\lambda}\Delta n \quad (1) \qquad \Delta\theta_{pp} = \frac{1}{2}\arcsin\left[\frac{\Delta I_{pp}}{I_0}\right] \quad (2)$$

evaluated from eq. 2 where pp denotes peak-to-peak values of induced tilt and intensity modulation. In the smectic C*-phase, the tilt angle was determined by applying a low-frequency field, and seeking the two extinction orientations by rotating the sample between crossed polarizers.

## Results and discussion

The polymer under investigation exhibits chiral A- and C-phases. We first consider the electro-optics in the A*-phase, where the electroclinic effect (16) manifests itself in a fast and linear switching. The effect is basically a field-induced tilt angle in the orthogonal A*-phase. For small applied electric fields and not too close to the A*-C* transition, the induced tilt varies linearly with the field, eq. 3, where $e_c$ is the electroclinic coefficient given by eq. 4. Here $T_c$ is the temperature of the A*-C* transition, $\alpha$ is the first constant in the Landau free-energy expression, and $\mu$ is the structural coefficient. One characteristic of the

$$\theta = e_c E \quad (3) \qquad e_c = \frac{\mu}{\alpha(T-T_c)} \quad (4) \qquad \tau = \frac{\gamma_\theta}{\alpha(T-T_c)} \quad (5)$$

electroclinic effect is the field independence of the response time, which is given by eq. 5 where $\gamma_\theta$ is the viscosity coefficient for the $\theta$-motion. The values of the response times are in the sub-millisecond range for polymer VI (fig. 3d), which is about hundred times longer than for low molar mass compounds. As can be seen from eq. 5, there is a critical slowing down close to the C*-phase, where the response time gets very long. At the same time the induced tilts, eq. 4, become large. This behaviour, illustrated in fig. 2, is typical close to a paraelectric-ferroelectric phase transition. The electroclinic coefficient $e_c$ can be regarded as a susceptibility, following a general scaling law

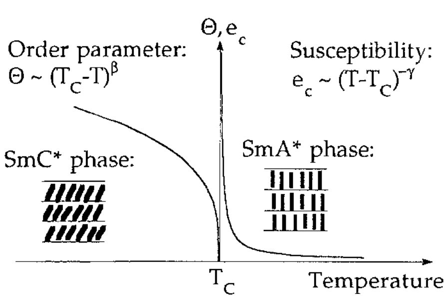


**Figure 2.** The order parameter and its susceptibility at a second order phase transition.

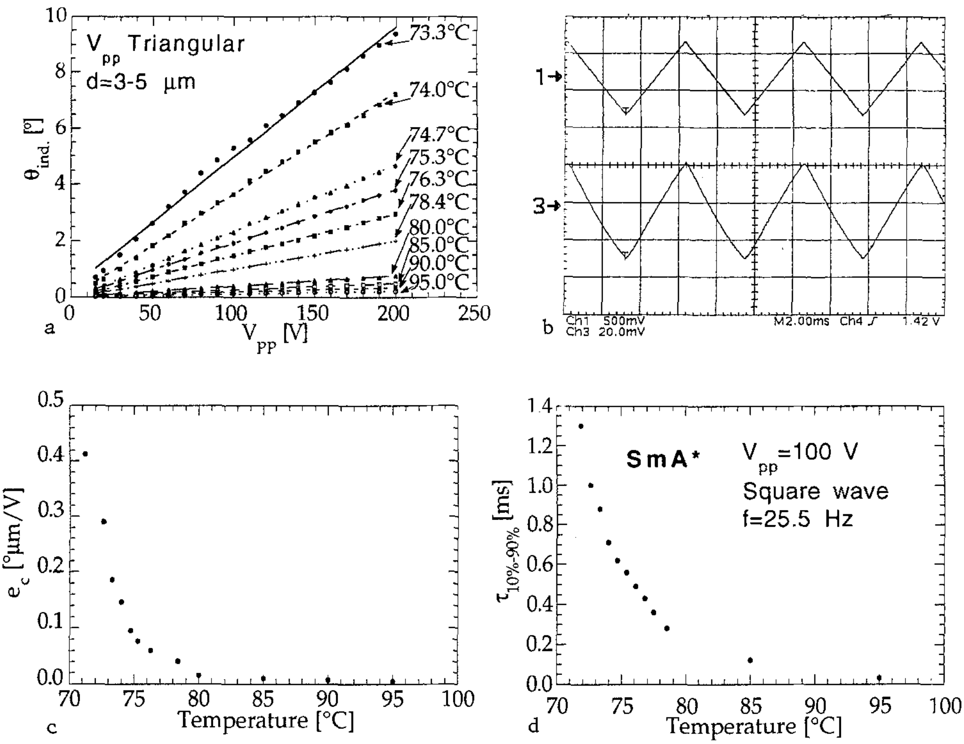


**Figure 3.** SmA*-phase. *a.* Induced tilt angle (eq. 3). *b.* Linear optical response on applied electric field at 80.0°C. *c.* Electroclinic coefficient (eq. 4). *d.* Optical response time (eq. 5).

(17) (fig. 2) of which eq. 4 is the special case $\gamma=1$ from mean field theory. The dielectric susceptibility also shows this behaviour near the transition. The experimental data on $e_c$ for polymer VI (fig. 3c) yield a different value of $\gamma$ at a first simple curve fitting, and therefore requires further analysis. In a temperature region near the A*- C* transition, the switching is more complicated, leading to field-dependent switching times and a saturation effect in the induced tilt. The electroclinic effect is present in all chiral A-phases with intrinsic or doped chirality, and has also been observed in other orthogonal phases (e.g. smectic B). For polymers, it has so far been reported in only a few cases.

Let us now consider the electro-optics of the ferroelectric smectic C*-phase of polymer VI. The tilt angle (fig. 4a) is found to follow the scaling law of the order parameter given in fig. 2, though the determination of $\beta$ is uncertain from the present data. The optical response (fig. 4b, trace 3) on the applied triangular wave (fig. 4b, trace 1) reflects a typical smectic C* switching between the two tilt angle extremes yielding the optical analogue (fig. 4c) of the ferroelectric hysteresis loop. Decrease of optical response time with temperature is found (fig. 5), in this phase essentially a manifestation of decreasing viscosity. The optical response on an applied square wave field is shown in fig. 6 at three different temperatures. The time scale decreases by a factor of 10 between the chosen temperatures, and most notably the polymer switches at room temperature.

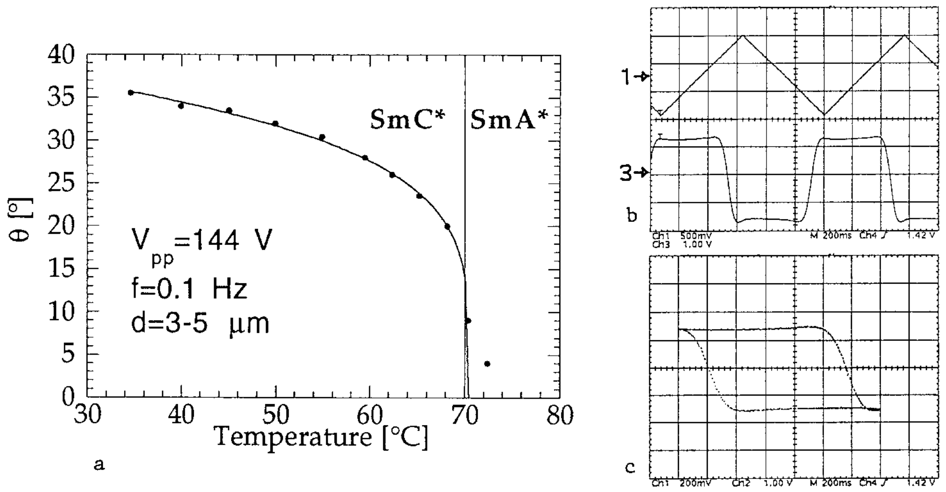


**Figure 4.** SmC*-phase. *a.* Tilt angle (order parameter) behaviour as in fig. 2. *b.* Typical ferroelectric optical response at 52.5°C. *c.* Optical hysteresis corresponding to *b.*

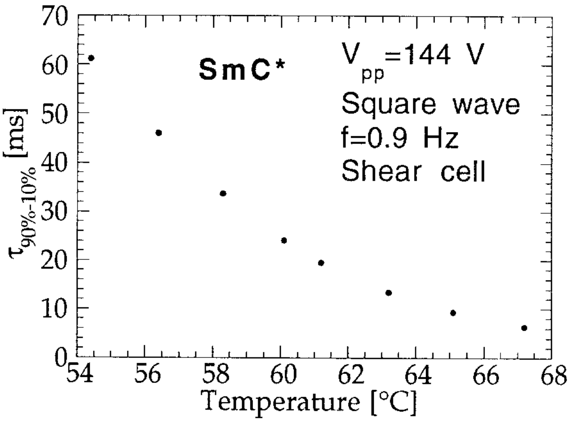


**Figure 5.** The optical response time versus temperature in the SmC*-phase.

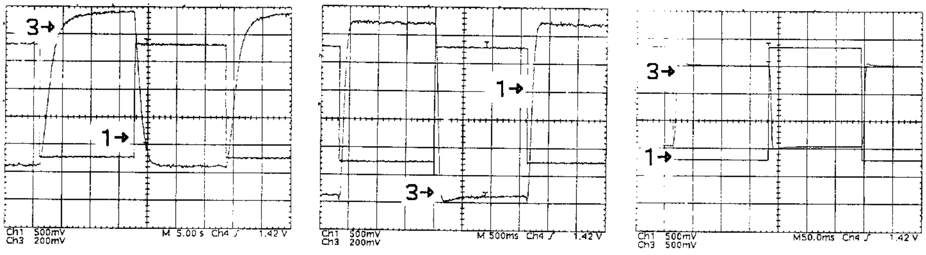


**Figure 6.** Optical switching at 23.7°C, 49.5°C and 68.0°C, respectively. Response times 2 s, 88 ms and 4 ms, respectively. Trace 1 = applied field, trace 3 = optical response.

In conclusion, a liquid crystalline polysiloxane with a new chiral mesogenic unit was synthesized. The polymer shows broad smectic C*- and A*-phases. Good alignment was obtained in shear cells and physical characterization was carried out demonstrating electroclinic effect in the smectic A*-phase, critical slowing down at the transition, and ferroelectricity in the smectic C*-phase. Electro-optical switching at room temperature was also observed. A full account of the work on this and related LC-polymers will be published elsewhere.

## Acknowledgements

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